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METHOD OF MAKING LONG LENGTH SUPERCONDUCTORS

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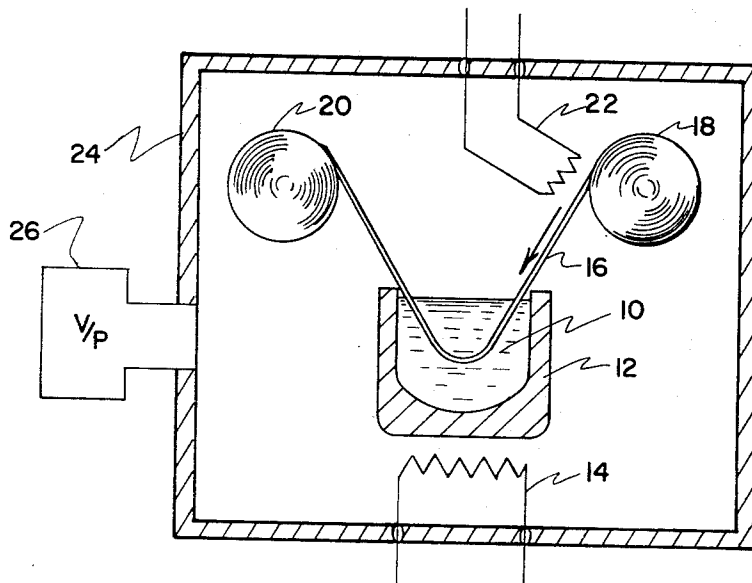


Fig.-1

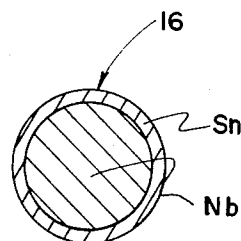


Fig.-2

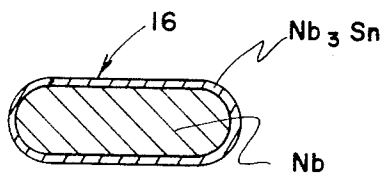


Fig.-3

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METHOD OF MAKING LONG LENGTH SUPERCONDUCTORS

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ABSTRACT OF THE DISCLOSURE

Long lengths of hard superconductor—niobium stannide or vanadium gallide—are prepared by running a long wire of the niobium or vanadium through a molten bath of the tin or gallium, respectively, very rapidly to form a thin coating, then electroplating to build up the coating to a desired thickness, then flattening the wire to ribbon form and finally heating for diffusion.

The present invention relates to superconductors, particularly in the form of elongated wires or ribbons which can be wound into solenoids or used as long transmission lines.

A principal difficulty in the commercial application of superconductivity is that the materials having the best electrical properties under high magnetic fields—niobium stannide and vanadium gallide—are very difficult to fabricate on a production line basis. Several new methods have been devised for overcoming these difficulties, with respect to niobium stannide; these are described in U.S. Patent 3,124,455, to Kunzler and Buehler, copending application S.N. 133,653, of Allen and Stauffer, and now abandoned, and copending application S.N. 207,320, of Allen, Das and Stauffer, now U.S. Patent No. 3,218,693.

It is the principal object of the present invention to provide a new method of forming niobium stannide superconductors which is particularly suitable for very long lengths.

It is a further object of the invention to provide a long superconductor which is easy to insulate.

It is a further object of the invention to provide a process of making a niobium stannide superconductor which has improved reliability and economy compared to the prior art processes.

Finally, it is an object of the invention to provide a manufacturing process for long superconductors comprising vanadium gallide.

In general, the present invention contemplates the passage of a niobium wire through a tin bath or a vanadium wire through a gallium bath to form a primer coat which is uniform and highly adherent. Then the coat is adjusted to a desired thickness by plating. The wire is then cold rolled to flatten it to the form of a ribbon with rounded edges. Such a ribbon is readily coated with plastic insulation compared to prior art ribbons with sheared edges. The final ribbon form is particularly suitable because it has greater resistance to certain modes of field penetration than a wire. Yet, in the present process the ribbon is not formed until after coating and plating steps which might tend to create twists in a ribbon and pose other handling problems.

The invention accordingly comprises an improved process of forming superconductive niobium stannide and vanadium gallide superconductors and the products of said process, characterized by an improved structure.

For a more detailed explanation of the invention, as applied in a preferred embodiment, reference should be had to the following discussion, taken in connection with the accompanying drawings wherein:

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FIG. 1 is a schematic view of a vacuum coating apparatus;

FIG. 2 is a schematic, cross-section of a tin coated niobium wire; and

FIG. 3 is a schematic cross-section of a flattened stannide-coated niobium wire.

Referring now to FIG. 1, molten tin 10 is held in a graphite pot 12 and heated by a heater to a temperature of 700° C.—900° C., temperatures above 750° C. being preferred. When the tin temperature is less than 800° C., a heater 22 is used to pretreat the wire to a dull red to clean the wire before dipping. If the bath temperature is 800–900° C., preheating is unnecessary. Niobium wire, .0005" to .025" in diameter is fed from a roll 18 through the molten tin at a rate of about 100 feet per minute for a residence time in the molten tin of less than one second. If the bath temperature is 700–800° C., the wire is fed at 50–100 feet per minute. If the bath temperature is 800–900° C., the wire is fed at 100–200 feet per minute. The coated niobium wire is wound into roll 20. This coated niobium wire shown in cross-section in FIG. 2 comprises a uniform, bright adherent tin coating with a thickness of about .0001 inch.

The coating process is carried out in a vacuum chamber 22 evacuated by convention vacuum pumping system 26 to a pressure of less than .0001 mm. Hg. The coating could also be carried out under an atmosphere of an inert gas with similar purity.

After the coating step, the chamber 22 is air released and the coated wire is passed through an electroplating bath to adjust the final thickness of the coating by addition or removal of tin. The initial dip coating serves as an excellent primer coat to insure ease of plating and uniformity of plating thickness. The coated wire is then cold rolled flat to a ribbon form having a thickness of about one-tenth to one-third the original wire diameter.

The ribbon is then treated with a separating agent, and coiled into a tight spool. The spool is heat treated in a muffle furnace, under an atmosphere of purified argon, at 950° C. for 1–4 hours. At the end of the heating step, the muffle is water cooled and cut open. The spool can be unwound and the ribbon can be subsequently wound into a solenoid, rotor coil, or other desired shape. At this stage the ribbon will have the cross-section form indicated in FIG. 3. The central core of niobium will be free of substantial diffusion and the coating will comprise an intermetallic alloy having the characteristic Nb₃Sn crystal structure. Other elements may be substituted for tin in the lattice, as taught in the work of Saur, copending application S.N. 307,896, filed Sept. 10, 1963, now Patent No. 3,244,490. This can be accomplished by dissolving alloying additions in the molten tin 10 (FIG. 1). It is also possible to strengthen the niobium substrate without adversely affecting the formation of an intermetallic superconductive coating or the ductility of the final coated ribbon. For instance, 1–5% by weight of zirconium or titanium can be alloyed with niobium in-forming the original wire 16 supplied on spool 18.

Referring again to FIG. 3, it is seen that the edges of the final ribbon are rounded. This avoids the possibility of cutting through an interleaved plastic insulation foil when winding solenoids. It also makes it possible to directly coat the ribbon with a plastic insulation by passing through a bath or through extrusion or heat shrinking techniques. The plastic adheres easily to the rounded edge.

Example

Tin (Vulcan extra pure—99.999%) was melted and maintained at 750° C. in a graphite pot in a vacuum chamber using the procedure outlined above. A spool of 0.010" diameter niobium wire was unwound in the

chamber, fed through the molten tin bath and rewound. The chamber was air released and the tin coated wire was examined inch by inch, under a microscope. No bare spots were found. The wire was repeatedly flexed, yet the coating remained adherent. Separate sections of the wire were then electroplated in a stannous fluoborate bath at 6 volts to deposit additional tin in amounts of (a) .0001", (b) .0002", (c) .0003", (d) .0004", (e) .0005", (f) .0006", and (g) .0016" thickness. The separate pieces were then flattened by a rolling mill to produce ribbons about .0025" thick by .045" wide with rounded edges. The ribbon sections were straight.

After heat treatment, the ribbons were bent around test probes and current was passed through them while they were under liquid helium temperatures and external magnetic fields, applied perpendicular to the widths of the ribbon. The critical current of the ribbons were comparable to those obtainable from clad ribbons of comparable size.

Very long lengths of niobium wire can be obtained in comparison to available lengths of ribbon formed directly from niobium ingots or powder compacts. Thus, the present invention has particular application to requirements where lengths of over 3,000 feet are necessary. Where necessary, wire lengths of 3,000-5,000 feet can be welded end to end to form wires in excess of 30,000 feet. The composite wire can be coated, as disclosed, with assurance of continuity and uniformity of coating. After electroplating, the composite wire can be rolled to produce a straight ribbon suitable for heat treating and subsequent fabrication into solenoids and the like, with or without insulation.

The process of the present invention can also be applied to the production of vanadium gallide diffusion layers on a vanadium ribbon. This is particularly important since gallium is more difficult to handle than tin and the vanadium gallide superconducting alloy is more brittle than the niobium stannide.

Vanadium wire is treated in a gallium bath and then plated as in the tin coating of wire. Bath temperatures of 700-800° C. are used for the gallium bath. An important difference is that the vanadium wire is removed to a protective atmosphere of argon or nitrogen after dipping to form the primer coat of gallium. Exposure to contaminant gases such as oxygen is avoided in transferring the vanadium wire from the molten gallium bath to the plating bath. During the rolling step, the rolls are water cooled to remove heat from the gallium coating.

The vanadium and gallium can be doped with small amounts of other materials such as silicon to form ternary vanadium gallide alloys in the diffusion coating. The heat treating step is carried out as described above with respect to niobium stannide.

What is claimed is:

1. A method of preparing a superconductive niobium stannide ribbon comprising the steps of continuously feeding a niobium wire having a length in excess of 3,000 feet through a molten tin bath maintained at a temperature between 700° C. and 900° C. under a contaminant-free atmosphere whereby the wire is uniformly coated with

tin, subsequently cold rolling the wire to flatten it to a ribbon having a thickness between $\frac{1}{10}$ and $\frac{1}{2}$ the original wire diameter and rounded edges, heat treating the ribbon to react the tin coating with the niobium ribbon to form a diffusion layer of niobium stannide at the surface of the ribbon whereby the ribbon demonstrates a critical temperature of about 18° K. wherein the tin coated wire is subjected to an electroplating step after dipping to control the final thickness of the coating.

2. The method of claim 1 wherein said stannide coated ribbon is further coated with a plastic to form an insulation completely covering the ribbon.

3. A method of preparing a superconductive niobium stannide ribbon comprising the steps of precleaning and continuously feeding a niobium wire having a length in excess of 3,000 feet through a molten tin bath maintained at a temperature of between 700° C.-800° C. at a rate between 50-100 feet per minute to provide a residence time in the molten bath of less than one second, during which time a thin coating of tin is formed on the wire, the said precleaning and feeding through a molten bath being conducted under vacuum, subsequently electroplating an additional tin coating on the dip coated wire to provide a uniform tin coating with a thickness on the order of one mil, cold rolling said wire to a ribbon having a thickness less than half the original wire diameter, and having rounded edges, heat treating the cold formed ribbon under an inert atmosphere at a temperature of 900-1000° C. for one to four hours to form a diffusion layer of niobium stannide at the ribbon surface having a thickness of 0.1-0.5 mil, whereby a long ductile ribbon having a uniform coating of superconductive niobium stannide having a critical temperature of about 18° W. is produced.

4. A method of preparing a superconductive vanadium gallide ribbon comprising the steps of feeding a vanadium wire at least 5 mils in diameter through a molten gallium bath maintained at a temperature between 700° C. and 900° C. under vacuum to provide a uniform primer coat of gallium on said vanadium wire, then feeding said coated wire to a protective atmosphere of inert gas, subsequently electroplating gallium on said coated wire to build up the coating thickness to 0.5-1 mil, the electroplating being carried out under a protective atmosphere of inert gas, subsequently cold rolling said plated wire to form a ribbon having rounded edges and a thickness less than half the wire diameter, removing heat from the wire during the cold rolling, then heat treating the plated ribbon to form a diffusion coating of vanadium gallide having a critical temperature of about 16.5° W.

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